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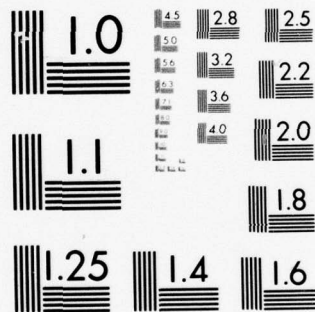
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ABSTRACTS

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1977 AFOSR CONTRACTORS MEETING ON COMBUSTION AND PLUME KINETICS

APRIL 4-5, 1977

ARNOLD AIR FORCE STATION
ARNOLD ENGINEERING DEVELOPMENT CENTER
TULLAHOMA, TENN.

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Compilation of
Abstracts -
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COMBUSTION AND PLUME KINETICS
4-5 April 1977.

9 Interim rept.

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15 AF-AFOSR-2644-74

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April 4-5, 1977

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Arnold Air Force Station
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AGENDA

1977 AFOSR COMBUSTION AND PLUME KINETICS MEETING

Sunday
3 Apr 77

- 1930 - Bus from Nashville Airport to Motel
- 2100 - Bus from Nashville Airport to Motel

Monday
4 Apr 77

- 0800 - Bus from Motel to AEDC (A & E Building)
- 0815 - Registration
- 0845 - Welcome - AEDC Dr. William Heiser
Chief Scientist
- 0900 - Welcome - AFOSR Dr. Brian Quinn
Director Aerospace Sciences
- 0915 - Laser Fluorescence Measurements of F. E. Hovis, J. Finzi,
Vibrational Energy Transfer in Water C. Bradley Moore
and Ammonia University of California,
Berkeley
- 0945 - Hydrocarbon Oxidation and Pyrolysis F. L. Dryer, R. A. Santoro,
Studies in a Turbulent Flow Reactor and I. Glassman
Princeton University
- 1015 - Coffee
- 1030 - Comparison of Models and Experiments D. M. Golden
for Radical-Radical Combination Reactions Stanford Research Institute
- 1100 - Chemical Kinetic Interests of AFAPL Captain T. Rosfjord
Wright-Patterson
- 1130 - Interfacial Chemical Reactions in Flow D. E. Rosner
Systems Yale University
- 1200 - Lunch

1300	-	Studies of Ignition Delay — The Early Stages of Combustion	S. H. Bauer Cornell University
1330	-	Kinetics of Hydrocarbon Oxidation Reactions	R. R. Baldwin Hull University
1400	-	Combustion Kinetics of Selected Aromatic Hydrocarbons	R. C. Farmer, R. A. Matula, Louisiana State University
1430	-	A Plan for Evaluated Rate Constant Data	N. Cohen K. Westberg Aerospace Corporation
1500	-	Tour of AEDC Facilities	
1630	-	Bus to Motel	
1730	-	Bus from Motel to Officers Club	
1745	-	Cocktails	
1830	-	Banquet	
2030	-	Bus to Motel	

Tuesday
5 Apr 77

0800	-	Bus from Motel to AEDC	
0830	-	Kinetics Interests of AFAPL	D. Mann AFRPL-DYS, Edwards
0900	-	Collisional Activation of Water Radiation	J. Fenn Yale University
0930	-	Kinetic Reaction Coefficients in Rocket Plumes	W. R. Snow, L. D. Schearer, K. J. Nygaard University of Missouri Rolla
1000	-	Coffee	
1030	-	Ion-Ion Neutralization Rates	J. R. Peterson Stanford Research Institute
1100	-	Spectroscopic Measurements on High-Temperature Species	W. Weltner, Jr. University of Florida

1130	-	CO Analysis in Combustion Gases	B. Krakow, H. Scott Arnold Engineering Development Center
1200	-	Lunch	
1300	-	Kinetics of Metal ATom Oxidation Reactions	A. Fontijn AeroChem Research Laboratories, Inc.
1330	-	Kinetics of Aircraft and Rocket Plume Constituents	F. P. Tully and A. R. Ravishankara Georgia Institute of Technology
1400	-	General Discussion	
1445	-	Bus to Motel	
1500	-	Bus from Motel to Nashville Airport	
1630	-	Arrival Nashville Airport	

LASER FLUORESCENCE MEASUREMENTS OF VIBRATIONAL ENERGY TRANSFER IN
WATER AND AMMONIA

F.E. Hovis, J. Finzi and C. Bradley Moore

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Water vapor is an extremely efficient vibrational energy relaxer, both with itself and with other molecules. Thus, besides being a problem of fundamental interest in chemical kinetics, relaxation rates of water are important in determining the gas dynamics of and the radiation emitted by many combustion systems, particularly exhaust plumes from air-born vehicles.

In a set of experiments done on vibrational energy transfer, a Nd-YAG pumped optical parametric oscillator provides a coherent source of tunable infrared radiation which is used to excite either the symmetric (100) or asymmetric (001) stretch of H_2^{18}O . By an appropriate choice of interference filters and gas filter cells, fluorescence from the stretching levels, the bending overtone level (020), or the bending overtone and fundamental (010) levels combined may be observed. The resulting signal-averaged fluorescence traces have been analyzed to give the total deactivation rate constants for the stretching, bending overtone, and bending fundamental levels. A set of experiments is also done using argon as a collision partner.

Analysis of the (001) fluorescence shows that (001) and (100) are coupled and relax together with a rate constant $k_s = (7.4 \pm .7) \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}$. Argon is found to be about 200 times less effective in deactivating the stretches. A similar analysis of (020) fluorescence gives a rate constant for deactivation of $k_2 = (3.0 \pm .4) \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}$, with argon again being about 200 less effective. The decay of fluorescence from the (020) and (010) levels together gives limits on the deactivation rate constant for the (010) level of $1.8 \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1} < k_1 < 3.0 \times 10^6 \text{ sec}^{-1} \text{ torr}^{-1}$.

By comparing the relative total fluorescence from (010) and (020), it is possible to extract some qualitative information on branching ratios. It is found that the deactivation of (020) has significant contribution from both the near-resonant process $\text{H}_2\text{O}(020) + \text{H}_2\text{O}(000) \rightarrow 2\text{H}_2\text{O}(010)$ and the $V \rightarrow T, R$ process $\text{H}_2\text{O}(020) + \text{H}_2\text{O}(000) \rightarrow \text{H}_2\text{O}(010) + \text{H}_2\text{O}(000)$. In addition, it is concluded that in stretching level deactivation, the channel going to (020) predominates.

Future experiments on deactivation of H_2^{16}O require the higher laser powers which will be provided by a new parametric oscillator system that will be completed within the next few months. Relaxation of the bending vibration of NH_3 will be studied in the intervening time using a CO_2 TEA laser.

HYDROCARBON OXIDATION AND PYROLYSIS STUDIES
IN A TURBULENT FLOW REACTOR

F. L. Dryer, R. A. Santoro, and I. Glassman
Aerospace and Mechanical Sciences
Princeton University, Princeton, N. J. 08540

Since the last Contractor's Meeting, much has been accomplished in the Princeton program. The new flow reactor which uses plasma heating of the carrier gas has been completed and is in operation. The agreement of the data obtained with this reactor and with the older one in which a packed bed is used to heat the carrier is excellent, much better than could have been expected, and is further verification of the utility of the turbulent flow reactor technique for kinetic measurement. Also numerical modeling of the methane and carbon monoxide oxidations in the turbulent flow reactor predicts well the experimentally obtained composition profiles. These results are still further support of the technique and conceptual benefits to be obtained from the overall kinetic correlations developed.

Work on the oxidation of ethane has been completed. As previously reported our results show that there are apparently three sequential and overlapping regimes in hydrocarbon combustion. In the first regime, the aliphatic is converted primarily to the olefin; in the second the olefin is converted primarily onto carbon monoxide and water; and lastly the CO is oxidized to CO₂.

For ethane some interesting overall results have been found. The following correlations have been found for the fuel lean regime.

$$-\frac{d[C_2H_6]}{dt} = 10^{14.38 \pm 0.28} \exp(-52250 \pm 2500/RT)$$

$$[(C_2H_6)_0 - (C_2H_6)]^{0.8} [C_2H_6]^{0.4} [O_2]^{-0.1}$$

Region 1

$$-\frac{d[C_2H_6]}{dt} = 10^{9.9 \pm 0.43} \exp(-45950 \pm 2110/RT) [C_2H_6]^{0.8}$$

Region 2

The stoichiometric fuel rich regime is characterized as

$$-\frac{d[C_2H_6]}{dt} = 10^{13.41 \pm 0.45} \exp(-39210 \pm 2500/RT) [C_2H_6]^{0.8} [O_2]^{0.75}$$

for both regimes.

The explanation of the dual value of ethane oxidation depicted by the above correlations lies with the extent of hydroperoxyl radical formation leading to an autocatalytic effect via hydroxyl radical attack on the primary fuel. The absolute concentration of the oxygen determined whether HO₂ plays

an important role in the temperature regime of the experiments and helps delineate between the fuel rich and fuel lean conditions.

Initial results on propane oxidation show that because of the additional step of propyl radical decomposition that there are some differences in the modeling of Region 1. Some very preliminary results on the oxidation of benzene will also be discussed.

COMPARISON OF MODELS AND EXPERIMENTS FOR RADICAL-RADICAL
COMBINATION REACTIONS

David M. Golden

Stanford Research Institute, Menlo Park, California 94025

Values of rate constants for radical-radical combination reactions and the reverse bond scission unimolecular processes as functions of temperature and pressure are becoming available for increasingly complex systems.^{1,2} These data along with thermochemical values³ compose a nicely over-determined system. Reaction models can be tested to the limits of the accuracy of these data.

Approaching the problem with the hope of developing models easily extrapolated to large systems, which at the same time do not violate the increasingly well understood detailed physical understanding currently being developed,⁴ has led us to an RRKM approach based on a "hindered rotational" model for the temperature-sensitive transition state.⁵

We will report some data on the combination reactions of saturated and unsaturated hydrocarbon radicals and discuss them in terms of the above model.

Also to be discussed are reactions of atmospheric interest, such as $\text{OH} + \text{NO}_2$, $\text{ClO} + \text{NO}_2$, and $\text{HO}_2 + \text{NO}_2$. The same model has been applied⁶ to simple proton transfer reactions as well, since these often proceed through proton-bound dimers in a manner exactly analogous to radical combination.

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(b) K. Y. Choo, P. C. Beadle, L. W. Piskiewicz, and D. M. Golden, *Int. J. Chem. Kinetics*, 8, 45 (1976).
(c) D. M. Golden, K. Y. Choo, M. J. Perona, and L. W. Piskiewicz, *Int. J. Chem. Kinetics*, 8, 381 (1976).
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3. S. W. Benson, Thermochemical Kinetics, 2nd Ed., John Wiley and Sons Inc., New York, 1976.
4. M. Quack and J. Troe; *Ber. Bunsenges, Physik. Chem.*, 78, 240 (1974); 79, 170 (1975); 79, 469 (1975).*
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6. W. N. Olmstead, M. Lev-On, D. M. Golden, and J. I. Brauman, *J. Amer. Chem. Soc.*, 99, 0000 (1977).

CHEMICAL KINETIC INTERESTS OF AFAPL

Captain T. Rosfjord
Fuels and Lubrication Division
Air Force Aero Propulsion Laboratory, WPAFB

Historically, the Air Force Aero Propulsion Laboratory (AFAPL) was responsible for the development of air-breathing propulsion concepts, including not only the engine hardware but also the necessary support power systems and the fuel. Within the past year, the Laboratory has also acquired a responsibility for fundamental investigations of the various aspects of air-breathers. Of course, in fulfilling this role, AFAPL coordinates very closely with AFOSR. The research topics to be discussed are those for which additional chemical kinetic information is required. As appropriate, a time scale will be applied to those needs. It must be noted, however, that the characteristic time to transition ideas from fundamental investigations to the inventory is measured in decades. Three areas will be specifically addressed—alternate fuels, high density fuels for volume limited systems, and the apparent discrepancy between optical and probe measurements of NO_x .

The first NO_x area stems from the coupled increased cost, decreased availability problems associated with jet fuels derived from petroleum crude supplies. It is recognized that alternate sources must be developed, and that fuels refined from them will likely have physical and chemical properties different than current fuels. The manner in which the fuel variables affect the steady state and transient combustion processes and pollutant formation rates needs to be investigated.

The second area recognizes the need to increase the chemical energy per unit volume of fuel for volume limited systems. Current fuel development efforts have resulted in mixtures of hydrogenated dimers of norbornadiene commonly referred to as RJ5, which has approximately 30% more energy per volume than JP4. Essentially no reaction kinetic studies of this fuel have been performed. While this lack of knowledge does not pose a limitation for current systems (fluid mechanic processes are rate controlling) future developments of supersonic combustion could accentuate the need for an improved kinetic understanding.

The third area concerns an apparent discrepancy in measured nitric oxide emissions as determined by conventional probing and optical techniques. This problem was first noted by workers at AEDC in 1972 as they probed a jet engine afterburner exhaust with a UV absorption technique, and noted NO_x concentrations five times greater than corresponding probe measurements. Subsequent studies have shown similar trends, although the magnitude of the discrepancy was dependent upon the reacting environment. As well, recent investigations by Samuelsen at the University of California, Irvine, indicate that probe influences can dramatically reduce the NO_x concentration that would be measured at its exit. These types of studies raise serious questions about the accuracy of probe and optical measurements, and computational schemes based on such measurement.

INTERFACIAL CHEMICAL REACTIONS IN FLOW SYSTEMS

Daniel E. Rosner

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 Department of Engineering and Applied Science
 New Haven, Connecticut 06520 USA

This program deals with two broad research areas of energy conversion/aerospace interest; viz. i) the intrinsic kinetics of gas/solid interfacial chemical reactions leading to gasification, dissolution and/or recombination; and ii) coupled chemical and physical phenomena in multiphase flow systems. Recent progress and plans for each of the following specific problems will be discussed verbally, and in the corresponding references cited below:

- a) Determination of chemical energy accommodation coefficients for N-atom association on metals up to 2600K (Pt, Ir, Rh, Pd, W, Re, Co)¹
- b) Determination of N-atom recombination coefficients on pyrographite, silicon carbide and alumina at temperatures up to 2300K²
- c) Determination of elementary rate constants and energetics of the N/Ta and N/Nb interactions at temperature up to 2800K^{3,4}
- d) Development of quantitative criteria for the onset of "group" behavior (flame sharing) in the combustion of fuel droplet arrays⁵

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2. Sau, R., Halpern, B. and Rosner, D. E., "High Temperature Kinetics of Surface-Catalyzed Nitrogen Atom Association on Pyrographite, SiC and Al₂O₃", J. Chem. Soc. Faraday Transactions I. Physical Chemistry (submitted March 1977).
3. Feng, H. H. and Rosner, D. E., "Resistance Relaxation Kinetic Studies of High Temperature Tantalum and Niobium in Dissociated Nitrogen Atmospheres 1. Methodology, Dissolution/Exsolution Mechanisms and Kinetic Inferences from Steady-State Behavior", J. Chem. Soc. Faraday Transactions I. Physical Chemistry (submitted April 1977).
4. Feng, H. H. and Rosner, D. E., "Resistance Relaxation Kinetic Studies of High Temperature Tantalum and Niobium in Dissociated Nitrogen Atmospheres 2. Kinetics and Energetics of Chemisorption, Interface Crossing, Associative Desorption and Interstitial Diffusion", J. Chem. Soc. Faraday Transactions I. Physical Chemistry (submitted April 1977).
5. Labowsky, M. and Rosner, D. E., "Conditions for 'Group' Combustion of Droplets in Fuel Clouds: I. Quasi-Steady Predictions", Proc. Symp. on Evaporation/Combustion of Fuel Droplets, American Chemical Society (Advances in Chem. Series) (in press, 1977).

STUDIES OF IGNITION DELAY --- THE EARLY STAGES OF COMBUSTION

S. H. Bauer

Department of Chemistry, Cornell University, Ithaca, New York 14853

We are utilizing the laser-schlieren technique for measuring density gradients close to shock fronts, and thus determine the endo/exothermic balance during the early stages of reactions which are initiated by incident shock waves. For example, in the pyrolysis of methane we not only determined the rate constant for the first step [$\text{CH}_4 + \text{Ar} \rightarrow \text{CH}_3 + \text{H} + \text{Ar}$; $k_1 = 1.0 \times 10^{17} \exp(-85.8 \pm 1/RT)$], but also demonstrated that to account for the recorded profile of the post shock density gradients, eight additional reactions must be inserted. While for several of these reliable rate constants are available, the rates for the others had to be adjusted to generate an adequate fit. Thus we obtained a quantitative check on the mechanism operating during the early stages of pyrolysis --- a regime which had previously not been readily accessible to investigation. We now have evidence that the direct production of ethylene occurs via: $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$: $k_4 \sim 1 \times 10^{13} \exp(-52/RT)$.

We also investigated the early stages of hydrocarbon oxidation by recording the shape of the laser-schlieren curve for various $\text{CH}_4/\text{O}_2/\text{Ar}$ mixtures. The endo/exothermic balance during the "dark" period (ignition delay) permitted us to check on the critical reactions which initiate hydrocarbon oxidation and to introduce a mechanistic criterion for this characteristic time. In one temperature regime we noted the appearance of oscillations; these impose sharp criteria on the model. Work is continuing in this area.

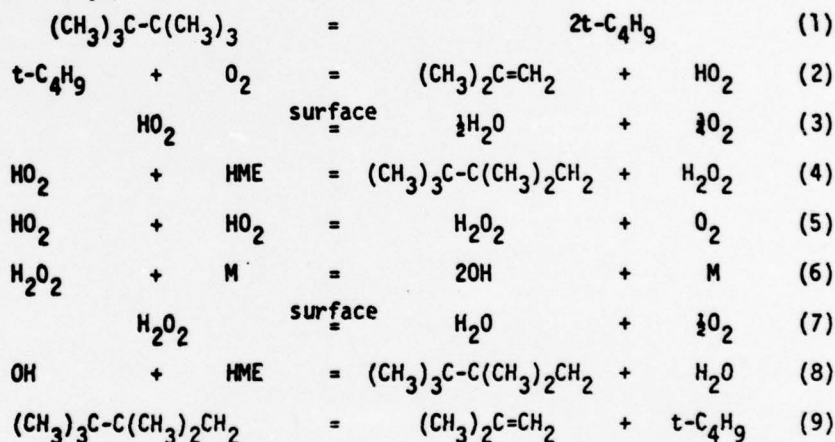
Finally, our shops are completing the construction of a revised flow reactor-QMS unit, in which we incorporated good gas dynamic design for reliable sampling of transient species from a controlled reaction zone. The special features include fast pumping and easily interchangeable sampling orifices to match a wide range of reactor pressures. Reactions can be initiated via injected streams of atoms, in flames, electrical discharges or by laser pyrolysis.

MECHANISM OF HYDROCARBON OXIDATION*

R. R. Baldwin and R. W. Walker

Chemistry Department, The University, HULL, England

To complement existing methods of studying the elementary reactions involved in hydrocarbon oxidation, the decomposition of hexamethylethane (HME) has been studied to examine its potential as a source of both t-butyl radicals and of HO₂. Calculations show that the reaction of HME with O₂ is at least 1000 times slower than the decomposition reaction (1) in the temperature range 400 - 540°C and at pressures of O₂ up to 1 atmosphere, and this is confirmed by the fact that the rate of decomposition of HME is independent of O₂ concentration over a ten-fold range.

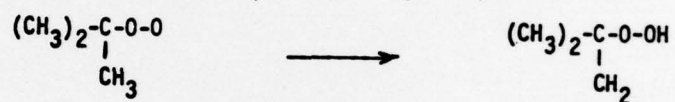


In the presence of O₂, t-C₄H₉ radicals react predominantly according to equation (2), as indicated by the very high yield (ca. 98%) of isobutene. Use of a KCl-coated surface reduces the formation of H₂O₂ by reactions (4) and (5) because of the efficient surface destruction of HO₂ radicals by reaction (3); this surface also destroys H₂O₂ by reaction (7), so that chain propagation by reactions (6) and (8) is minimised. Allowance for the small residual chain reaction gives the expression $k_1 = 6.0 \times 10^{16} \exp(-69400 \text{ cal mol}^{-1}/\text{RT}) \text{ s}^{-1}$. Combination with data for the reverse reaction gives $\Delta_f H_{298}^0(\text{t-C}_4\text{H}_9) = 10.5 \pm 1 \text{ kcal mol}^{-1}$. This suggests a bond dissociation energy for t-Bu-H some 2-3 kcal mol⁻¹ above currently accepted values.

* Grant No. AFOSR-73-2450

Mechanism of Hydrocarbon Oxidation / continued

The variation of the ratio [isobutene oxide]/[isobutene] with temperature is used to obtain an activation energy of $35 \pm 3 \text{ kcal mol}^{-1}$ for the isomerisation of the t-butylperoxy radical into the t-butylhydroperoxyalkyl radical.



COMBUSTION KINETICS OF SELECTED AROMATIC HYDROCARBONS

Richard C. Farmer and Richard A. Matula
College of Engineering, Louisiana State University
Baton Rouge, Louisiana 70803

The primary objective of the research program is to develop an understanding of the high temperature pyrolysis, oxidation and carbon formation processes in selected aromatic hydrocarbon-air combustion systems. The results of this study can be subsequently utilized to optimize the use of high aromatic content synthetic jet fuels in both present and new generation jet combustors. The specific objectives of the research are to: (1) study the kinetics of aromatic hydrocarbon pyrolysis in temperature and pressure ranges of interest in jet turbine combustors; (2) study the ignition and oxidation of aromatic hydrocarbon-air systems in temperature and pressure ranges of interest in jet turbine combustors; (3) measure the critical fuel/oxidizer equivalence ratio for incipient soot formation in aromatic hydrocarbon-air mixtures at temperatures and pressure ranges of interest in jet turbine combustors; and (4) develop quasi-global and/or detailed oxidation mechanisms for selected aromatic hydrocarbons based on the results of the experimental data and computer modeling of the reaction systems. The aromatic fuels to be considered during the study will include fuels that vary in the number of ring structures and the degree of saturation.

The program includes a balanced effort encompassing both experimental work and analytical mechanistic modeling phases. An integrated experimental program will provide a description of reaction rates from which mechanism schemes and important elementary rate constants can be determined. A mathematical model of these mechanism processes will be developed.

The experiments will be carried out in the existing conventional shock tube and the existing single-pulse shock tube in LSU's combustion laboratory. All of the thermochemical, gas dynamics and chemical kinetics computer programs required for successful completion of the program are presently available.

A PLAN FOR EVALUATED RATE CONSTANT DATA

Norman Cohen and Karl Westberg
Aerospace Corporation

The field of chemical kinetics has matured rapidly in the past decade or two. The growing body of data and derived rate coefficients that have been published in journals, technical reports, and symposia has generated a need for bibliographies and reviews to aid the practicing kineticist and also the engineers who are not kineticists but need to use kinetic data.

These user aids have taken several forms: (1) Bibliographies of references pertaining to a given reaction; (2) Non-critical tables of published rate coefficients; (3) Critical reviews in tabular or data sheet format; (4) In-depth critical monographic reviews of individual reactions or groups of reactions. For the experienced kineticist, all four of these formulas can be useful in different cases. For the engineer, only the third type is useful, and even then most of the published tables leave much to be desired.

In sharp contrast, the field of thermochemistry has a standard, widely accepted and utilized reference to which specialist as well as engineer turns whenever the need arises: The JANAF Thermochemical Tables. An immense success, they are used extensively by scientists and engineers throughout the defense community as well as by other technical personnel around the world. The existence of these Tables has ensured that thermochemical data of interest are evaluated only as needed by scientists especially competent to do so, rather than many times by different users who may or may not be competent to perform such an evaluation.

There are several reasons why the JANAF Tables are so popular: (1) they are continually updated; (2) they are published in a standardized, compact format that makes them easy to use; (3) they contain references to the original literature (the NBS Thermochemical Tables, which contain no such references, are not nearly so popular); (4) experimental results are reanalyzed as necessary; (5) calculations are made where data are sparse; for example, vibrational frequencies and moments-of-inertia are commonly calculated; (6) the scientists who generate the tables are accepted as competent and authoritative.

In spite of the inherent differences between kinetics and thermochemistry, we nevertheless feel that a similar set of tables of kinetic data would be of great use to the scientific and engineering community--without eliminating the need for the other types of aid enumerated above.

We propose to establish a set of chemical kinetic reference data sheets similar to the JANAF Thermochemical Tables. These data sheets would be more than a mere compilation of data; on the other hand, they would not entirely replace critical reviews, either in tabular or prose format. All data would be critically evaluated and original experimental results reanalyzed as necessary. Each data sheet will contain a brief discussion of how the analysis was performed together with pertinent experimental data and calculations. We envision that for the majority of the reactions to be evaluated that a brief discussion of this sort is all that any scientist or engineer would require. However, there are quite a few important reactions or groups of reactions for which there are large amounts of experimental data that will require extensive reanalysis with considerable supporting calculations. We foresee that many kineticists would like to see the details of such analyses and calculations rather than just a brief summary of them. This calls for separately published in-depth critical reviews to supplement the data sheets. As part of this program we will generate such reviews, except when an adequate review is already in the literature.

Kinetics of Interest to the
Air Force Rocket Propulsion Laboratory

David M. Mann
Air Force Rocket Propulsion Laboratory
Edwards Air Force Base, CA

The determination, verification and compilation of specific kinetic reaction rates are of fundamental interest to several activities at the Air Force Rocket Propulsion Laboratory. Calculation of performance and signature of engines relies heavily upon high quality, basic Kinetic rate data. In addition, continued proposals for new and exotic propellant types generate fresh demands for modeling and prediction. Specific recommendations for reaction Kinetic studies to support current and anticipated AFRPL needs will be presented.

Cross Sections for T-V Excitation of CO₂
from Measurements of Consequent Infrared Radiation

Subbarao Ryali and John B. Fenn - Yale University
C. E. Kolb - AeroDyne Research, Inc.

After an extensive study we have recently achieved some modest success in determining cross sections for excitation of ground state of CO₂ molecules to radiating states by collisions with N₂ and H₂ molecules at translational energies in the several eV range. The idea is that two opposed free jets are set far enough apart so that they comprise in effect two uncollimated molecular beams. Their molecules thus encounter each other in an interaction region where the densities are so low that each molecule in one of the jet flows undergoes at most a single collision with a molecule from the opposed jet flow. By aerodynamic acceleration with hydrogen or helium and control over the source temperature, the effective center of mass collision energies can be varied over a fairly wide range. A sensitive infrared detector "looks" at the interaction region and responds to photons radiated from molecules which have been collisionally excited.

We use two axisymmetric sonic nozzles which are 100 microns in diameter. They are positioned 9 cm apart in a chamber which is 80 cm in diameter and 100 cm long, evacuated by an oil diffusion pump 80 cm in diameter. The nominal pumping speed of 3×10^4 liters per second is halved by a freon cooled baffle. The pumping speed is such that we can use source pressures up to 1500 torr while maintaining background pressure at a few times 10^{-5} torr. The detector is a high impedance photovoltaic chip of Indium Antimonide (InSb), .04 cm² in area. A silicon lens with a transmission of 0.21 focusses the radiation on the detector from a collision volume of about one cubic centimeter. The flow from one of the nozzles is chopped at a frequency of 200 hertz in order to take advantage of increased signal-to-noise provided by tuned amplifiers and phase sensitive detection. The detector and all the surfaces which it sees are cooled to liquid nitrogen temperatures.

For the asymmetric stretch mode of CO₂, the photon wavelength is 4.3 microns corresponding to a threshold energy of 0.288 eV. For this wavelength, the overall response of the detection system, including the amplifiers, is 2.48×10^9 volts/watt. The noise is such that we can achieve an effective output sensitivity of about one millivolt corresponding to an input of 4×10^{-13} watts. Under these conditions we have been able to detect radiation from CO₂ excited by collisions with H₂ and N₂ molecules. An analysis of the data indicates that the excitation cross sections for T-V exchange range from 6.6×10^{-19} cm² to 1.7×10^{-16} cm² and for V-V exchange range from 3.4×10^{-17} cm² to 1.7×10^{-15} cm² depending upon the identity of the collision partners and the collision energy. Further, experimental data on N₂/CO₂ collisional activation of CO₂(v₃) mode strongly indicates a) T-V rather than V-V excitation, b) N₂/CO₂ T-V excitation cross sections for CO₂ (v₃) mode depend strongly upon collisional energy -- as anticipated, c) form of differential scattering cross section assumed for vibrationally activated molecules has strong influence on magnitude of derived cross sections.

Future experimental plans include: 1) switching the nozzle geometry from 180° to 90° for better defined interaction volume; 2) continuing $\text{CO}_2 + \text{X} \rightarrow \text{CO}_2^\dagger + \text{X}$ experiments with $\text{X} = \text{N}_2, \text{O}_2, \text{H}_2, \text{CO}_2, \text{Ar}, \text{He}$ and H_2O ; 3) performing $\text{H}_2\text{O} + \text{X} \rightarrow \text{H}_2\text{O}^\dagger + \text{X}$ with X as above.

KINETIC REACTION COEFFICIENTS IN ROCKET PLUMES

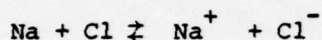
W. R. Snow, L. D. Schearer, K. J. Nygaard
University of Missouri-Rolla, Rolla, Missouri

Pergament and Jensen developed a model for afterburning in solid fuel rocket plumes in which the electron concentration as a function of distance along the plume axis depends critically on reactions involving the production of free electrons by ion pair production in a potassium-chlorine collision followed by associative detachment of Cl^- with atomic hydrogen, and on the loss of free electrons by three body recombination of electrons with K^+ and three body attachment of electrons to atomic chlorine. Further development of the model predictions depends on better measurements of rates for these reactions. Progress on experiments to measure these reactions will be reported. Drift tube measurements of dissociative attachment of electrons in HCl will be discussed and a rate constant recommended. A complicating factor in these experiments was the rapid clustering of Cl^- to HCl . A rate constant for this process in excess of $10^{-26} \text{ cm}^6/\text{sec}$ was measured. The possible significance of cluster ions in the plume will be discussed. A crossed beam technique is being used to study ion pair production in K-Cl collisions. A fast beam of potassium atoms from a seeded nozzle beam source crosses a target beam of chlorine atoms formed by thermal dissociation in an effusive oven source and ions produced at the intersection of the beams are counted. Progress on this experiment will be reported. Progress will also be reported for an experiment to measure the three body recombination rate for electrons with K^+ by observing the decay constant of light from the $8P - 6S$ transition in the recombination spectrum of potassium. In this experiment the initial K^+-e plasma is formed by two photon absorption from a dye laser beam passing through the potassium vapor. The method recently has been demonstrated to work for cesium in our laboratory.

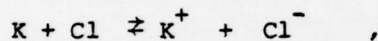
ION-ION NEUTRALIZATION RATES

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In the absence of satisfactory experimental determination of the backward and forward rates for



and



R. E. Olson at SRI has performed quantum close-coupling calculations of the cross sections. Coupling matrix elements between reactant and product states were derived from pseudo-potentials. The collision energy-dependent cross sections are averaged over a Boltzman distribution to obtain rate coefficients

$$k = 8\pi\mu (2\pi\mu kT)^{-3/2} \int_0^\infty dE \cdot EQ(E) \exp(-E/kT).$$

At low energies the neutralization cross sections are proportional to $1/E$; the equation above leads to a $T^{-1/2}$ dependence of the rate at low temperature:

$$k = 4EQ(E) \cdot (\pi\mu kT)^{-1/2} .$$

The neutralization rates can be parameterized as

$$k(\text{K}^+ + \text{Cl}^-) = 3.1 \times 10^{-9} T^{-1/2} (1 + 2.6 \times 10^{-6} T^{3/2})$$

and

$$k(\text{Na}^+ + \text{Cl}^-) = 1.6 \times 10^{-7} T^{-1/2} (1 + 4.7 \times 10^{-7} T^{3/2})$$

with no dependence on the Cl^- fine structure states. The ionization rates are

$$k[\text{K} + \text{Cl}(^2P_{3/2})] = 2.2 \times 10^{-14} T^{1/2} (1 + 8400/T) \exp(-8400/T),$$

$$k[\text{K} + \text{Cl}(^2P_{1/2})] = 2.6 \times 10^{-14} T^{1/2} (1 + 7140/T) \exp(-7140/T),$$

$$k[\text{Na} + \text{Cl}(^2P_{3/2})] = 6.2 \times 10^{-13} T^{1/2} (1 + 17700/T) \exp(-17700/T),$$

and

$$k[\text{Na} + \text{Cl}(^2P_{1/2})] = 4.3 \times 10^{-13} T^{1/2} (1 + 16400/T) \exp(-16400/T) ,$$

all in units of cm^3/sec .

At 1800°K the $\text{Na}^+ + \text{Cl}^-$ recombination rate is $3.9 \times 10^{-9} \text{ cm}^3/\text{sec}$, and for $\text{K}^+ + \text{Cl}^-$ it is $8.8 \times 10^{-11} \text{ cm}^3/\text{sec}$. These rates are much smaller than those that have been obtained experimentally and theoretically for other species such as $\text{H}^+ + \text{H}^-$, $\text{O}^+ + \text{O}^-$, and for molecules. The reason for these low rates will be discussed.

SPECTROSCOPIC MEASUREMENTS ON HIGH-TEMPERATURE SPECIES

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Reactive metal oxide, hydride, fluoride, carbide, and nitride molecules produced at high temperatures in various environments are trapped in rare-gas solids and studied spectroscopically at 4°K. Optical and ESR spectroscopy yield vibrational, electronic, and magnetic (hyperfine and g tensors, zero-field-splittings) data which are combined with theoretical calculations (varying from crude to ab initio) and gas-phase observations (if existing) to provide a definitive picture of the vapor species. Large gaps still exist in our present knowledge of these molecules and of radicals formed from the lighter elements carbons, silicon, and boron.

CO ANALYSIS IN COMBUSTION GASES

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CO number densities and temperatures in gases are being determined using high resolution infrared absorption spectra of the CO fundamental and first overtone bands. The spectra are obtained with a high resolution Michelson interferometer. Integrated absorptances of single lines are extracted from the spectra and converted to CO partial pressures and temperatures using a curve of growth formula in which both pressure broadening and Doppler broadening are considered. Published line strength and pressure broadening parameters are employed.

The technique should be applicable to any molecule whose line structure can be resolved.

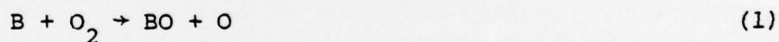
KINETICS OF METAL ATOM OXIDATION REACTIONS

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Several Air Force efforts require reliable kinetic data on the formation of metal oxidation products. Specifically: (i) data on boron and aluminum oxidation by halogen species and the subsequent shift reactions of the halides formed with (atmospheric) oxygen are needed for development of some advanced propulsion systems, and (ii) knowledge of magnesium and boron oxidation by O_2 is required for ramjet technology.

The High-Temperature Fast-Flow Reactor (HTFFR) technique, which is used in the present program, was developed specifically for measuring the kinetics of metal atom, Me, and diatomic metal oxide radical, MeO, oxidation reactions. The HTFFR is an adaptation of the conventional tubular fast-flow reactor, but it is suitable for the approximate temperature range 300 to 2000 K. The reaction mechanism and rate coefficient are obtained from measurement of relative Me or MeO concentration as functions of pressure, reactant concentration, flow velocity and temperature; these variables are independently controlled. Concentration measurements are made at observation ports near the downstream end of the reactor and are based on atomic resonance absorption and fluorescence for Me and laser-induced fluorescence for MeO.

The first reactions to be studied in this program are:



The contract was only recently initiated and there are as yet no results to report.

In the presentation the technique will be described, a summary of previous achievements obtained with it will be given, and the plans for study of Reactions (1) - (3) will be discussed.

KINETICS OF AIRCRAFT AND ROCKET PLUME CONSTITUENTS

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A new kinetics program, addressing both radical-hydrocarbon and metal atom reaction rate studies, is described. Central to these rate determinations is the technique of (laser/spark discharge) flash photolysis - (resonance/laser-induced) fluorescence.

The reactions of hydroxyl radicals with simple hydrocarbons are of great importance to the chemistry of combustion and plumes. Measurements of the rates of these reactions have, generally, been achieved in two separated temperature regimes. Direct measurements of absolute rate constants have been made between 240K-500K for many important OH-RH reactions using a wide variety of techniques. While these rate studies have typically been free from competing secondary processes, their limited temperature range has minimized their kinetic value to combustion and plume chemistry. In the high temperature regime relevant to combustion processes, rate data has been extracted from complex shock tube and flame studies. However, a comparison of Arrhenius extrapolations from these high and low temperature regimes for such key reactions as $\text{OH} + \text{H}_2$ clearly demonstrated the need for additional data in the intervening temperature range.

Measurements of the rate constants for reactions such as $\text{OH} + \text{H}_2$, CH_4 , CH_2O , ... between 500K-1200K represent a major thrust of our program. Our preliminary results on $\text{OH} + \text{H}_2$, CH_4 will be discussed, and the need to replace the existing resonance fluorescence detection system by laser-induced fluorescence detection will also be described.

Our studies on metal atom kinetics will initially focus on $\text{B}(\text{CH}_3)_3$. This molecule will be the first candidate examined as a potential pulsed kinetic source of boron atoms.

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR TR-77-0311	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) COMPILATION OF ABSTRACTS - 1977 AFOSR COMBUSTION AND PLUME KINETICS MEETING		5. TYPE OF REPORT & PERIOD COVERED INTERIM 4 April - 5 April, 1977
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s)		8. CONTRACT OR GRANT NUMBER(s) AFOSR 74-2604
9. PERFORMING ORGANIZATION NAME AND ADDRESS PRINCETON UNIVERSITY SCHOOL OF AEROSPACE & MECHANICAL SCIENCES PRINCETON, NEW JERSEY 08540		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 2308/B2 61102F
11. CONTROLLING OFFICE NAME AND ADDRESS AIR FORCE OFFICE OF SCIENTIFIC RESEARCH/NA Building 410, Bolling Air Force Base Washington, D. C. 20332		12. REPORT DATE April 1977
		13. NUMBER OF PAGES 27
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) CHEMICAL KINETICS COMBUSTION PLUME RESEARCH		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report is a collection of the abstracts of talks by contractors and grantees of the Air Force Office of Scientific Research (AFOSR) in the area of chemical kinetics related to combustion, plume and wake technologies at a meeting held at the Arnold Air Force Station, Arnold Engineering Center, Tullahoma, Tennessee, April 4, 5, 1977.		